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Radiative defects and optical response in oriented *para*-hexaphenyl films

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Abstract

The optical properties of an ordered *para*-hexaphenyl film, grown with molecules lying parallel to the substrate, are investigated. The absorption spectrum exhibits two peaks at 3.1 (L) and 4.35 (H) eV, featuring a different degree of polarization. The photoluminescence emission and the absorption at 3.1 eV are highly polarized. The presence of the L peak is strongly related to the growth conditions, and is favored at high deposition rates and low substrate temperatures. Upon 4.66 eV ultraviolet irradiation in air, the photoluminescence intensity and the absorption at 3.1 eV are reduced. Conversely, transitions at higher energies are almost unaffected by irradiation. Experimental data show that the L peak and emission arise from a crystal defect.

1. Introduction

Among π-conjugated materials, the *para*-hexaphenyl oligomer has attracted considerable attention as active layer in organic light emitting devices [1]. Due to the high blue electroluminescence quantum efficiency, *para*-hexaphenyl has been successfully exploited to obtain green and red light emission by using optical down conversion [1,2]. Homogeneous films can be prepared by molecular deposition. By varying growth parameters like substrate temperature and deposition rate, thin *para*-hexaphenyl layers with different orientations, morphology and degree of disorder are obtained [3a,3b,4,5]. The control of the molecular alignment with respect to the film surface is a key feature for improving device performances [6], the electrical and optical properties of π-conjugated films being strongly anisotropic. The formation of radiative defects is also of primary importance for an efficient light emission in these materials [7,8a,8b,9]. In fact, intermolecular interactions can lead to a splitting of the excited molecular levels in two (or more) exciton bands, the lowest of which is optically forbidden (or weakly allowed) in dipole approximation [10]. The understanding of the possible mechanisms inhibiting the quenching of the luminescence is a central point

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for the applications of oligomers in light emitting devices [9].

The high luminescence quantum yield of *para*-hexaphenyl films (up to 30%) clearly indicates the presence of efficient radiative decay channels. In specimens with significant short-range orientational disorder, a molecular-like optical response has been observed [11]. The purpose of this Letter is to study the optical response of an ordered film with the *para*-hexaphenyl molecules oriented predominantly along an axis parallel to the surface of a quartz substrate. This molecular alignment enables the excitation of electronic transitions with dipole moment both parallel and perpendicular to the oligomer axis, permitting an investigation of the anisotropic electronic properties of *para*-hexaphenyl films. In the viewpoint of applications, the deposition of molecules parallel to the substrate is quite important because it allows to achieve a significantly lower onset voltage for light emission and a higher current density at the same voltage than those obtained in electroluminescent devices with molecules standing on the substrate [6].

2. Experimental

Highly purified *para*-hexaphenyl was deposited by thermal evaporation onto the substrate at a pressure of 10^{-6} mbar. X-ray diffraction spectra have shown that by varying the deposition rate (0.08–100 Å/s) and the substrate temperature T_s (25°C–170°C) it is possible to realize samples in which molecular axes are oriented parallel (for high deposition rate and low T_s) or perpendicular (for low deposition rate and high T_s) to the substrate surface [3a,3b]. The sample we have examined was deposited on a quartz substrate at 10 Å/s and at room temperature, so the molecules are parallel to the substrate surface. The molecules are self-organized in a herringbone structure, with two non-translationally equivalent positions in the monoclinic cell. In order to obtain a preferential orientation, the evaporation process was stopped at a thickness of about 10 nm and the hexaphenyl surface was rubbed in air [12]. The rest of the film was evaporated on top of this surface which has grooves in one direction.

Luminescence was excited by the fourth harmonic of a pulse compressed Nd:YAG laser delivering 4-ps-long pulses or by the second harmonic of a synchronously pumped dye-laser delivering 0.5-ps-long pulses. Incident excitation intensities below 10^{10} photon/cm^2 were used. Temporal dispersion of the signal was achieved through a Hamamatsu optical sampling oscilloscope with a time resolution of 20 ps [11]. Absorption measurements at room temperature were carried out with a Cary 5E spectrophotometer in the range from 1.5 to 5 eV.

3. Results and discussion

Fig. 1 shows the absorption spectra of the oriented *para*-hexaphenyl film at 300 K. The spectra are shown for different orientation Θ between the electric field of the polarized incident light and the molecular axis. For polarization parallel to the

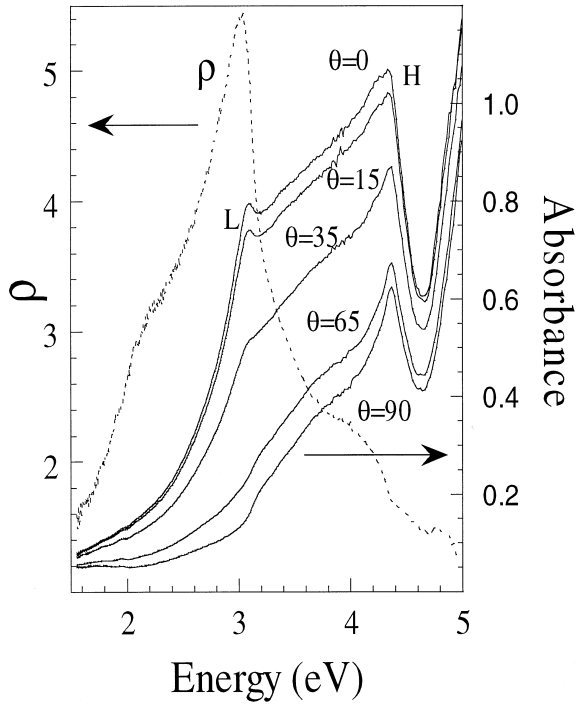

Fig. 1. Polarised absorption spectra of oriented *para*-hexaphenyl taken at different angles Θ between the electric field of the polarised incident light and the molecular axis. The polarization ratio ρ is also shown.

molecular backbone, two peaks appear at 3.1 and 4.35 eV, labelled in the following as *L* and *H*, respectively. *L* is not observed for perpendicular polarization. The polarization ratio ρ (defined as the ratio between the absorption in the parallel and perpendicular configurations) is also shown in Fig. 1. ρ exhibits two peaks close to *L* and *H*. The low energy peak is much more polarized ($\rho \sim 5$) than the high energy one ($\rho \sim 2$).

cw-Luminescence spectra polarized parallel and perpendicular to the molecular backbone are reported in panel (a) of Fig. 2. The two spectra are identical and consist of a main band at 2.94 eV, followed by a vibronic structure at 2.78 eV. The peak at 3.05 eV is presumably due to a crystal defect. Since the shape of the emission spectra does not depend on the polarization nor on the excitation energy, we can infer that only *one* type of luminescent centre is active in the sample. The intensity of the emitted light, polarized perpendicular ($I_\perp$) and parallel ($I_\parallel$) to the molecular backbone, is shown as a function of the angle Θ between the electric field of the polarized incident light and the molecular axis. This analysis has been done by using two different excitation energies, 3.29 and 4.66 eV, which are close to the *L* and *H* peaks, respectively. For both excitations, $I_\perp$ is almost independent of Θ. $I_\perp$ presumably originates from unoriented regions of the films. When the luminescence is excited by 3.29 eV, $I_\parallel$ is modulated according to the Malus law. The behaviour of $I_\parallel$ can be rationalised assuming that the emitting dipole oscillates mainly along the molecular backbone, suggesting that the absorption at the *L* peak and the emission arise from the *same* absorbing and radiative centre. The amplitude of the modulation is smaller when $I_\parallel$ is excited by 4.66 eV photons. For this excitation energy, excitations relax or migrate spectrally to the low energy level *L* prior to decay. The small modulation of the luminescence as a function of Θ therefore reflects the small absorption anisotropy at 4.66 eV.

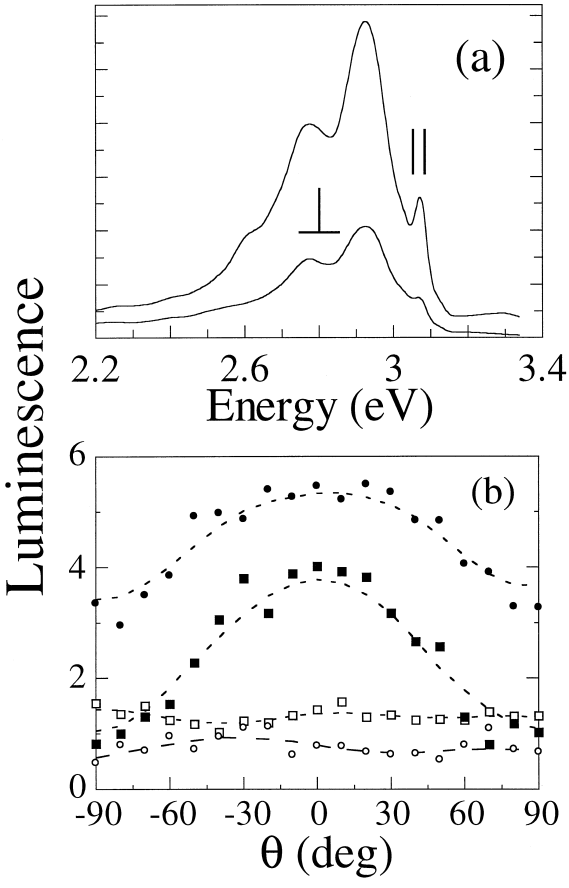

Fig. 2. (a) cw-Luminescence spectra polarized parallel ($I_\parallel$) and perpendicular ($I_\perp$) to the molecular axis. (b) $I_\parallel$ (full symbols) and $I_\perp$ (empty symbols) as a function of Θ, for 3.29 (squares) and 4.66 eV (circles) excitation energies, respectively.

The different nature of the electronic levels involved in the *L* and *H* transitions, as suggested by their different optical anisotropy, is further investigated by looking at the effects of UV irradiation on the intensity of the two transitions, when the sample is exposed to the air. We have excited different sample regions with 4.66 eV photons for times ranging from 0 to 90 min. Fig. 3 compares the absorption spectrum of a non-irradiated region with those of two zones irradiated for 45 and 90 min, respectively. The incident light was polarized parallel to the molecular axis. While *L* is reduced by about 40% after 45 min, the intensity of the *H* peak and of the higher energy transitions does not change significantly for this irradiation time. The spectrum measured after 90 min indicates that the sample was severely damaged by UV irradiation (this is also confirmed by a microscopic inspection of the film). These effects almost disappear in nitrogen atmosphere. It is important to note that after photo-oxidation, the luminescence intensity decreases, as shown in the insert of Fig. 3. Since UV irradiation weakly

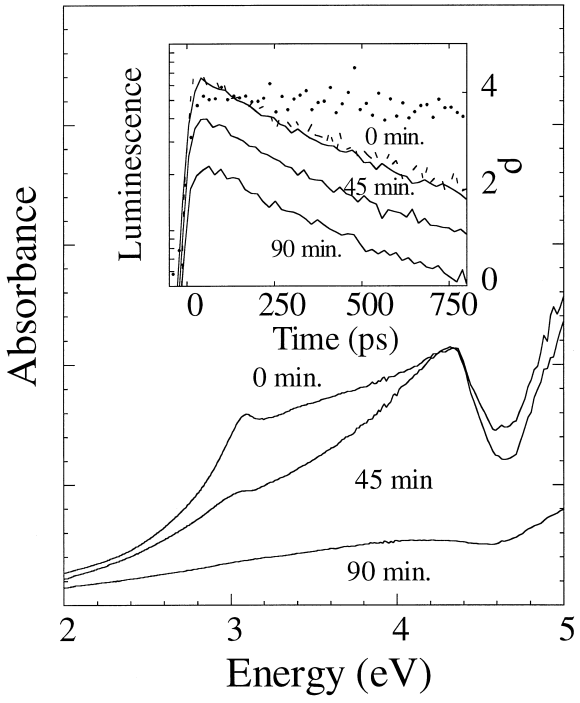

Fig. 3. Absorption spectra and luminescence temporal decays (inset) in sample regions irradiated by UV photons for different time intervals. In the insert, continuous (dashed) lines correspond to luminescence excited by 4.66 (3.29) eV photons, circles are the depolarisation ratio $\rho = I_{\parallel} / I_{\perp}$.

changes laser absorption at 4.66 eV, the reduction of the luminescence intensity excited by UV photons should be entirely ascribed to the quenching of the radiative centers. Finally, the decrease of the luminescence is strongly correlated to the decrease of the L peak, confirming that both emission and the lowest energy absorption peak involve the same electronic levels.

The L state, responsible for the high luminescence quantum yield of the oriented sample, can be attributed to a radiative trap, originated by positional disorder defects. The high degree of polarization of the emission suggests it arises from a vacancy [13]. The L level can be thought as due to the interaction between a defect and the lowest excitonic band. In the perfect crystal, the dipole moment of the transition to the lowest excitonic level resulting from the splitting of the lowest $\pi-\pi^*$ molecular transition is zero, as the dipole moments associated with the non-equivalent molecules compensate each other. The lack of one molecule in the elementary cell prevents this compensation, giving rise to a radiative centre around the vacancy. The resulting dipole moment is expected to oscillate along the direction of the molecular axis. The faster effect of photo-oxidation on L with respect to transitions at higher energies could be explained by the expected major oxygen content near vacancies. It is also important to remark that the growth parameters needed to get films with molecular axes parallel to the substrate, namely the low substrate temperature and the high deposition rate [3a,3b], favor the formation of crystal vacancies which give rise to a much more intense L peak in the absorption spectrum [4].

The inset of Fig. 3 reports the decay of the luminescence intensity excited by 3.29 and 4.66 eV photons, respectively. The emission lifetime is 500 $\pm$ 20 ps for both curves. The monoexponential character of the decay provides further support to the fact that the emitting states are localized. When the film is excited by 3.29 eV photons, the excitation and emission processes take place at the same radiative defect. For higher energy photons, absorption can occur away from the radiative centres. The signal rise time coincides, however, with the rise time of the experimental set-up, indicating a very short trapping time. The luminescence transients have been also recorded for emission polarized parallel and perpendicular to the molecular backbone. The depolarization ratio ρ does not vary with time, suggesting that excitations do not reach the boundaries of the crystal grains, where depolarization effects are expected. The long polarization memory time is in agreement with the fact that excitations are localized.

As shown in the insert of Fig. 3, even though the temporally integrated emission decreases with increasing irradiation time, the luminescence lifetime is weakly influenced by photo-oxidation. Conversely, similar studies in poly(*para*-phenylenevinylene) have shown that exposure to UV light under ambient air induces an increase of the number of carbonyl defects. Since they act as photoluminescence quenching centres the non-radiative decay rate is increased [14–16]. In *para*-hexaphenyl films, 3.29 eV photons generate excitons trapped around the radiative defects not quenched by UV irradiation. The effect of photo-oxidation is therefore to reduce the luminescence intensity, without changing appre-

ciably its temporal dynamics. When the film is excited by higher energy photons, excitations are trapped in a very short time so similar conclusions can be drawn.

In the *para*-hexaphenyl oriented films, molecules are organized in a herringbone structure in which orientation and distance between molecules are similar to those found in other oligomer films, where the influence of interchain interaction on the electronic and optical properties is important [17]. These similarities suggest that exciton coupling should be effective also in *para*-hexaphenyl. In defect-free regions of the crystal the lowest excitonic band is optically forbidden, so relaxation of excitations (or migration of excitation trapped at the L defect) toward these states should quench light emission. The high quantum yield of *para*-hexaphenyl indicates that the lowest excitonic level should be at higher energies with respect to the *L* state. Similar defect-induced levels giving rise to polarized emission have been also observed in hexathiophene crystals, just below the lower (weakly allowed) exciton level [13].

There are two indications from theory what the origin of the H feature could be. For α-sexithienyl single crystals it was shown by quantum chemical calculations in reference [18] that there is an optical transition around 1 eV above the absorption edge, which is due to the short-axis polarized 2^1B_u molecular excited state. For the corresponding polymer to *para*-hexaphenyl, the poly(*para*-phenylene), band structure calculations yield qualitatively the same result [19]: the absorption polarized perpendicular to the chain axis has its onset about 1 eV above the absorption polarized parallel to the chains. Both calculations also yield the fact that in the region of about 1 eV above the onset there is comparable absorption in both polarization directions – obviously then one would not expect a high degree of polarization.

4. Conclusions

In conclusion, we have studied the optical response of oriented *para*-hexaphenyl films with molecules parallel to the surface of a quartz substrate. We have shown that the high luminescence quantum yield and the lowest absorption peak *L* are due to radiative traps. The formation of such defects is correlated with growth parameters. Upon UV irradiation in air, light emission from radiative centres is strongly quenched, yielding to an effective decrease of the quantum yield. Localization of the photoexcitations is at the root of the exponential decay of the luminescence intensity, of the absence of any polarization memory loss, and of the weak influence of UV irradiation on the temporal dynamics. Experimental results indicate that the optical transition to the lowest exciton state of the defect-free crystal is forbidden in dipole approximation, as predicted by the Davydov theory of molecular excitons [10] and by more recent calculations in aggregates of π-conjugated oligomers [9].

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